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A Green Approach to Corrosion Inhibition of Aluminium in Acid Medium Using Azwain Seed Extract

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Abstract

The inhibition efficiency of different concentrations of Azwain seed extract on the corrosion of Aluminium in 0.5N HCl solution was investigated by weight loss method, electrochemical and surface analysis techniques. Results of weight loss method indicated a increase in inhibition efficiency (IE) up to a particular concentration of Azwain seed extract then a decrease on the samewith increasing inhibitor concentration. Polarization study revealed that Azwain seed extract controls both the anodic and the cathodic reactions. AC impedance spectra showed that a protective film is formed on the metal surface. The nature of the metal surface was analysed by Scanning electron microscopy (SEM). Adsorption of extract on the Aluminium surface was found to obey Longmuir and frumkin adsorptionisotherms. The thermodynamic parameters were calculated and discussed.

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Keywords: Aluminium metal, weight loss study, AC impedance spectra, thermodynamic parameters and SEM

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1. Introduction

Aluminum at present finds wide use in industries as well as in home appliances due to its lightweight, strength, durability and formability. Naturally, Aluminum is a highly reactive material. It has a very high attraction towards oxygen [1]. When a new Aluminum surface is exposed to air (or an oxidizing agent), it easily acquires a thin, compact, tightly adhering, self-healing film of Aluminum oxide (about 0,5µ in air). In non-stagnant water, thicker films (of hydrated oxide) are formed. Once the protective oxide layer is destroyed, the susceptibility of Al to attack is seen in oil well acidizing, pickling, cleaning and descaling operations where the metal is in contact with hydrochloric or sulphuric acids [2]. The use of chemical inhibitors has been limited because of the environmental threat. Due to environmental regulations, plant extracts are nowadays widely used as corrosion inhibitors.

The green inhibitors are the alkaloids and flavonoids and other natural products extracted from natural sources like plant. It can be done by simple procedures with low cost and also consists of synthetic compounds with negligible toxicity. Many corrosion control works have been performed using extracts of various plants as corrosion inhibitors [3-5].

Recently aqueous extracts of coriander seed extract [6], tritax procumbens [7], aningeria Robusta [8], bittercola extract [9], bitter leaf extract [10], cassia alata leaves [11], and cyanodon dactylon [12] have been used as corrosion inhibitors. The present work focuses on the inhibitory action of various concentrations of Azwain seed extract in controlling the corrosion of Aluminum in acid medium. The effect of temperature on the corrosion rate of Aluminum in presence of an optimum concentration of the Azwain seed extract was also studied and some thermodynamic parameters were also calculated.

2. Materials and methods

2.1 Preparation of Azwain seed extract

An aqueous extract of Azwain seed (Omam seed) was prepared by refluxing 40 g of Azwain seed with double distilled water, filtering the suspended impurities and making it up to 200 ml. This extract was then used as corrosion inhibitor in the present study.The major constituent of Azwain seed extract is Thymol, which is confirmed by UV and FTIR spectra

Analysis of UV and FTIR spectra

UV visible spectrum is recorded in water solvent using SHIMADZU 1800 UV double beam spectrophotometer. UV spectrum of the aqueous extract of PE is shown in fig.1(a). The absorbance around 260 – 273nm indicates the presence of a compound with a hetero atom Oxygen in the PE. A few drops of PE were dried on a glass plate. A solid mass was obtained. Its FTIR spectrum is shown below Fig.1(b). The O-H stretching frequency appears at 3442 cm^{-1}. The C=C stretching frequency is seen at 1643 cm^{-1}. The C-C stretching frequency appears at 1400 cm^{-1}. The C-O stretching frequency is located at 1109 cm^{-1}.Thus, the structure of PE is confirmed by FTIR spectrum.

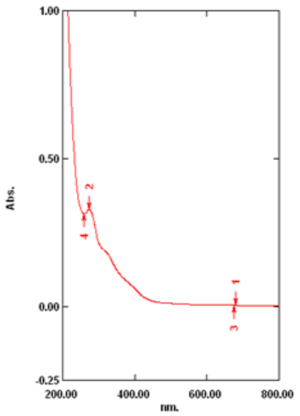


Fig. 1(a) UV spectrum of aqueous solution of PE

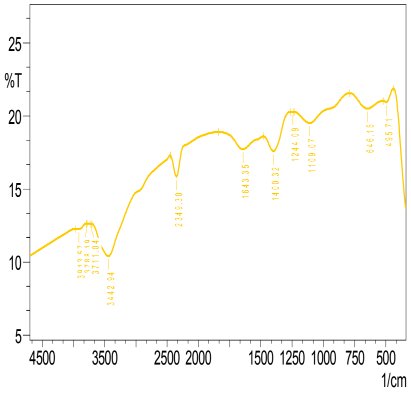
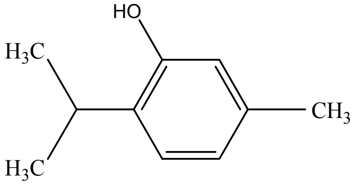


Fig. 1. (b) FT –IR spectrum of PE



Strcture of Thymol

2.2 Preparation of the specimen

Aluminium metals of dimensions 1.0 cm × 4.0 cm × 0.1 cm were polished to a mirror finish and degreased with acetone and used for the weight loss method and surface examination studies .

2.3 Weight-loss method

Aluminium metals were immersed in 100 ml of acid medium of normality 0.5NHCl containing various concentrations of the inhibitor (Azwain seed extract) for a period of 3 hours. The weights of the specimens before and after immersion were determined using a digital balance model AUY 220 SHIMADZU. The corrosion products were cleaned with acetone. The corrosion inhibition efficiency (IE) was then calculated using the equation (1)

$$IE = 100\,[1-(W_2/W_1)]\ \% \qquad (1)$$

where,

W_1 is the corrosion rate in the absence of inhibitor and W_2 is the corrosion rate in the presence of inhibitor. Corrosion rate (CR) was calculated using the formula (2)

$$CR = 534W / DAT \ \ \text{Mils per year (mpy)} \qquad (2)$$

where,

W = weight loss in milligrams D = density of specimen g/c = 2.70 gm/cm^3

A = area of specimen in square inches = 1.395 T = exposure in hours = 3hours

The degree of surface coverage (θ) was calculated from the weight loss measurement results using the following formula,

$$\text{surface coverage} = W_2 - W_1/W_1$$

where W_1 is the weight loss in the absence of inhibitor and W_2 is the weight loss in the presence of inhibitor.

2.4 Potentiodynamic polarization

Polarization studies were carried out in a CHI electrochemical work station with impedance model 608 E. A three - electrode cell assembly was used. The working electrode was Aluminium metal. A SCE was the reference electrode. Platinum was the counter electrode. From polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes anodic =βa and cathodic =βc were calculated and a linear polarization study was done. The scan rate (V/S) was 0.01. Hold time at E_f(s) was zero and quiet time (s) was two.

2.5 AC impedance spectra

The same instrument used for polarization study was used to record AC impedance spectra also. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies. Values of charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated.

$R_t = (R_s+R_t)-R_s$

where,R_s=solution resistance

C_{dl} value was calculated using the relationship

$$C_{dl} = 1/\ 2 \times 3.14\times R_t \times f_{max}$$

where, f_{max} = frequency at maximum imaginary impedance.

AC impedance spectra were recorded with initial E (v) = 0, high frequency (Hz) = $1\text{x}10^5$, low frequency (Hz) = 1, amplitude (V) = 0.005, and quiet time (s) = 2

2.6 Scanning Electron Microscopy (SEM)

The Aluminium metals were immersed in blank and in the inhibitor solution for a period of three hours was removed, rinsed with double distilled water, dried and observed through a Scanning Electron Microscope to examine the surface morphology. The morphology measurements of Aluminium metal were examined using a JEOL model 6390 computer controlled Scanning Electron Microscope.

3. Results and discussion

3.1 Weight loss study

The inhibition efficiency (IE) and the corresponding corrosion rate (CR) of various concentration of PE in acid medium are given in table 1. it is found that the IE increases up to a particular PE and then it decreases. When IE increases the corresponding corrosion rate also decreases. Maximum IE occurs for 9 ml of PE, with which further studies are carried out.

Table 1. Corrosion inhibition efficiency (IE) and the corresponding corrosion rates (CR) in (mills per year) of PE extract in controlling the corrosion of Aluminium in acid medium.

PE in ml	0.5N HCl	
	IE (%)	CR(mpy)
0	0	3.4499
2	67	1.5312
4	67	0.8979
6	70	0.6805
8	83	0.4773
9	90	0.2599
10	84	0.3922

3.2Analysis of Polarization curves

Polarization study has been used to detect the formation of protective film on the metal surface during corrosion inhibition process. The potentiodynamic polarization curves obtained for Aluminium metal in acid solutions in absence and presence of inhibitor (PE) system are shown in Fig.2. The electrochemical parameter such as corrosion potential (E_{Corr}), corrosion current (I_{corr}), Tafel slopes (βa and βc) liner polarization resistance (LPR) are given in Table 2. When Aluminium is immersed in 0.5N HCl solution, the corrosion potential is -0.6799 Vversus SCE. The formulation consisting of PE (9 ml) corrosion potential is shifted to -0.6784 V versus SCE. i.e., corrosion potential was not shifted significantly in presence of the extract suggesting that Azwain seed extract control both anodic and cathodic reactions to inhibit the corrosion of Aluminium by blocking active sites on the Aluminium surface. It indicates that PE is a mixed type inhibitor.

The corrosion current value and LPR value for 0.5N HCl are 7.788×10^{-4} A/cm^2 and 57.7 ohm cm^2.In the presence of inhibitor (9 ml PE) the corrosion current value decreased to 4.912×10^{-4} A/cm^2 and the LPR value increased to 88.8ohm cm^2. The fact that the LPR value increases with decrease in corrosion current indicates absorption of the inhibitor on the metal surface to block the active sites and inhibit corrosion and reduce the corrosion rate [12, 13].

Table 2. Corrosion parameters for Aluminium in 0.5N HCl solution in the absence and presence of inhibitor obtained by polarization method.

PE in ml	E_{Corr} V vs SCE	I_{Corr} A/cm2	βa V/dec	βc V/dec	LPR ohm cm^2
0	-0.6799	7.788×10^{-4}	4.679	7.800	57.7
9	-0.6784	4.912×10^{-4}	4.435	7.679	88.8

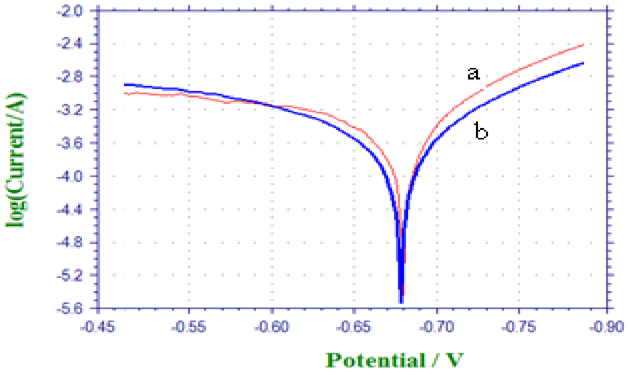


Fig.2 Polarization curves for Aluminium in 0.5N HCl solutions in the absence and presence of inhibitor. a) 0.5N HCl b) 0.5N HCl solutions containing 9 ml of PE.

3.3 Analysis of AC impedance spectra

Nyquist representations of Aluminium in 0.5N HCl solution in the absence and presence of inhibitor system are shown in figure 3. As shown in below Table 3, ac impedance spectra can be used to detect the formation of protective film on the metal surface. If a protective film is formed, the charge transfers resistance (R_t) increases and double–layer capacitance (C_{dl}) value decreases. The impedance parameters, namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in table 3. When the inhibitor is added to 0.5N HCl, R_t value is 45.25 ohm cm^2 and C_{dl} is 2.519×10^{-5} F/Cm^2. When 9 ml of Azwain seed extract is added R_t value increases from 45.25 ohm cm^2 to 70.33 ohm cm^2 and the C_{dl} value decreases from 2.519×10^{-5} F/cm^2 to 2.146×10^{-5} F/cm^2. This suggests that a protective film is formed on the surface of the metal [14, 15] as shown below Fig. 3.

Table 3. Impedance parameters of Aluminium in 0.5N HCl solution in the absence and presence of inhibitors obtained by AC impedance method.

System	Nyquist plot	
	R_t ohm cm^2	C_{dl} F/cm^2
0.5 N HCl	45.25	2.519×10^{-5}
PE (9 ml)	70.33	2.146×10^{-5}

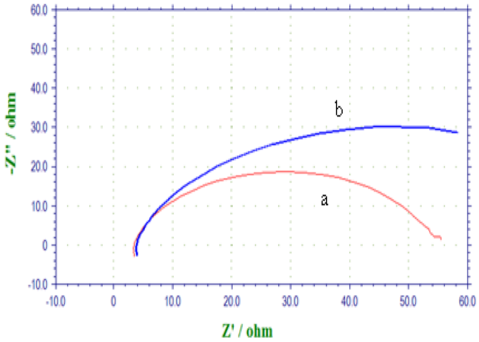


Fig. 3 AC impedance spectra for Aluminium in 0.5N HCl solutions in the absence and presence of inhibitor. a) 0.5N HCl b) 0.5N HCl solutions containing 9 ml of PE.

3.4Effect of temperature

The influence of temperature (303 K to 323 K) on weight loss of Aluminium metal in 0.5N HCl in different concentrations of inhibitor has been shown in table 4.Table 4 shows the IE and CR of Aluminium in 0.5N HCl in the presence of PE at different temperatures. From Table 4, it is clear that the IE and surface coverage (θ) increases with increasing inhibitor concentration (C) and decreases with increasing temperature from 303-323 K. The high surface coverage data also shows that the adsorption of PE at the Aluminium interface may be due to the electrostatic force between the atoms on the metal surface and the adsorbate (inhibitor molecules) [16]. Straight line graphs were obtained by plotting values of surface coverage θ versus values log C and C/θ values versus C, (Figure 4(a) and 4(b)), which is an indication of obeying and Langmuir adsorption isotherms [17] .

Table 4. Effect of temperature on the IE of PE

PE in ml	303 K			313 K			323 K		
	IE (%)	Θ	CR (mpy)	IE (%)	θ	CR (mpy)	IE (%)	θ	CR (mpy)
1	65	0.65	0.22	46	0.46	0.34	29	0.29	0.45
2	67	0.67	0.21	48	0.48	0.33	32	0.32	0.43
3	69	0.69	0.19	50	0.5	0.32	37	0.37	0.40
4	69	0.69	0.19	54	0.54	0.29	38	0.38	0.39
5	72	0.72	0.17	58	0.58	0.26	45	0.45	0.34
6	75	0.75	0.16	61	0.61	0.25	46	0.46	0.34
7	76	0.76	0.15	61	0.61	0.25	50	0.5	0.32
8	79	0.79	0.13	65	0.65	0.22	55	0.55	0.28
9	88	0.88	0.08	73	0.73	0.17	60	0.6	0.25

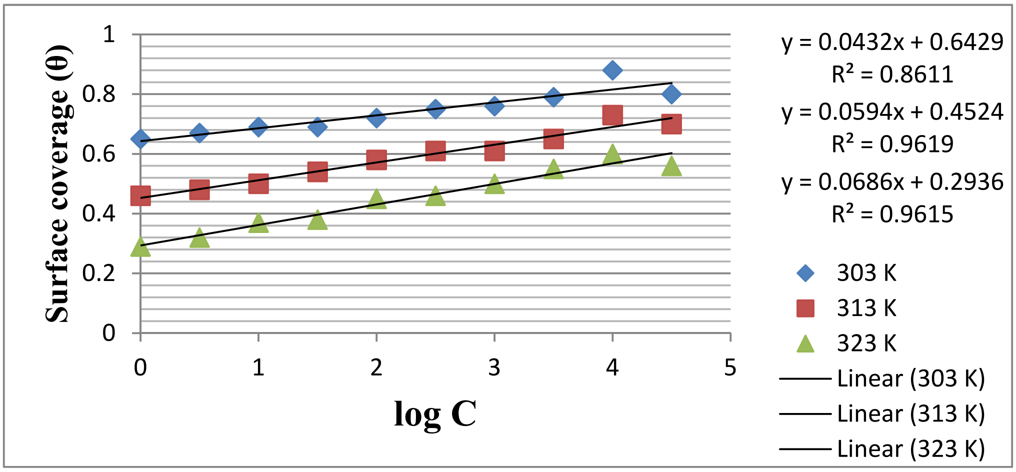


Fig.4 (a) Frumkin adsorption isotherm plotted as “θ” versus log “C” for Aluminium corrosion in 0.5N HCl containing various concentrations of PE at 303 K to 323 K.

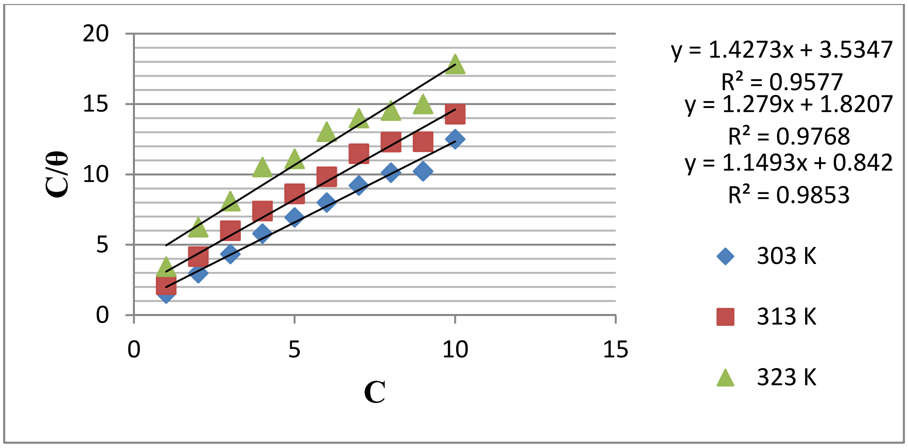


Fig.4 (b) Langmuir isotherm plotted as “C/θ” versus “C” for Aluminium corrosion in 0.5N HCl containing various concentrations of PE at 303 K to 323 K.

3.5 Thermodynamic parameters

The Arrhenius equation (3) was used to calculate the activation energy, E_a for corrosion reaction of Aluminium in various concentrations of inhibitor.

$$\log (p_2/p_1) = E_a/ 2.303R [1/T_1 - 1/T_2] \qquad (3)$$

where p_1 and p_2 are corrosion rates at temperatures T_1 and T_2 respectively, and R is gas constant.

The heat of adsorption (Q_{ads}) of inhibitor on surface of Aluminium was determined using equation (4). [18]

$$Q_{ads} = 2.303 R [\log (\theta_2/1- \theta_2) - \log (\theta_1/1- \theta_1)] \qquad (4)$$

where θ_1 and θ_2 are degree of surface cover ages at temperatures T_1 and T_2.

The values of free energy of adsorption $\Delta G_{ads,}$ of inhibitor on Aluminium surface were evaluated using equation (5). [19]

$$\Delta G_{ads} = -2.303 RT \log (55.5K) \qquad (5)$$

The values of activation energy (E_a), heat of adsorption (Q_{ads}), and free energy adsorption (ΔG_{ad}) for the inhibitor is given in table 5. Activation energy of PE varies between 72.37 KJ/mol and 141.61 KJ/mol. The results prove that E_a, increases as inhibitor concentration increases. The higher E_a values in inhibited solutions indicate that extracts mechanically block the active sites of Aluminium surface and decrease the surface area available for corrosion as shown in below Table 5.

The negative values of heat of adsorption, Q_{ads} varying from -61.46 kJ/mol to-78.69 kJ/mol for PE indicating the adsorption of inhibitor and thereby the inhibition efficiency decreases with temperature increases, is an evidence for the proposed physisorption mechanism [20].

The negative values of ΔG_{ads} confirm that the adsorptions of PE on the metal surface are spontaneous. This also favours physisorption ($\Delta G_{ads} < 40$ KJ/mol) [20]. When the ΔG_{ads} values are around -20 KJ/mol or less negative, it supports physisorption and when it is around -40 KJ/mol or more negative, it confirms chemisorption [21].

Table 5. Values of thermodynamic parameters for adsorption of PE on surface of Aluminium in 0.5N HCl.

E in ml	Activation energy, E_a (KJ/mol)	Heat of adsorption Q_{ads} (KJ/mol)	Free energy change ΔG_{ads} (KJ/mol) of adsorption at 303 K	Free energy change ΔG_{ads} (KJ/mol) of adsorption at 313 K
1	72.37	-61.46	-12.06	-10.03
2	78.57	-62.16	-12.29	-10.25
3	78.24	-63.10	-12.54	-10.45
4	79.41	-50.45	-12.54	-10.87
5	84.78	-49.03	-12.91	-11.29
6	85.76	-51.36	-13.31	-11.62
7	86.69	-55.63	-13.45	-11.62
8	90.14	-55.67	-13.90	-12.06
9	141.61	-78.69	-15.64	-13.04

3.6 SEM Analysis of metal surfaces

SEM images of magnification 500 of Aluminium metal was immersed in 0.5N HCl for 3 hours in the absence and presence of inhibitors system are shown in fig. 5(b) and 5(c) respectively. The SEM micrographs of the polished Aluminium metal surface (control) are shown in fig. 5(a). It shows the smooth surface of the metal and absence of any corrosion products formed on the metal surface. Fig. 5(b) denotes the SEM micrograph of Aluminium metal immersed in 0.5N HCl. The metal surface is rough, which indicates the corrosion of Aluminium in 0.5N HCl.

Fig. 5(c) indicates that in the presence of 9 ml of PE in 0.5N HCl, the surface coverage increases, which in turn results in the formation of insoluble complex on the surface of the metal (Al^{3+} - Thymol complex). The surface is covered by a thin layer of inhibitor that controls the dissolution of Aluminium metal [22, 23].

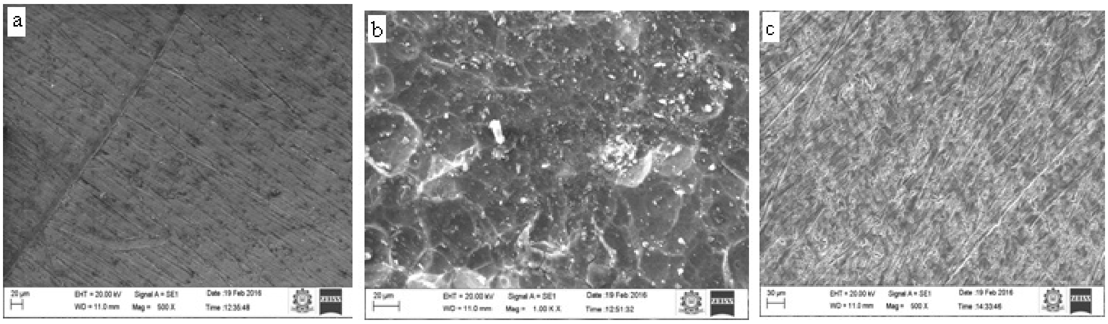


Fig. 5. SEM micrographs of

a) Polished Aluminium metal (control)

b) Aluminium metal immersed in 0.5N HCl

c) Aluminium metal immersed in 0.5N HCl containig 9 ml of PE.

4. Conclusion

The results of weight-loss study show that the formulation consisting of 9 ml of PE has 90% IE in controlling the corrosion of Aluminium in 0.5N HCl.Polarization study reveals that the PE controls both anodic and cathodic reaction. Hence it indicates that PE acts as a mixed inhibitor.IE and degree of surface coverage decreases as temperature increases.E_a increases as concentration of inhibitor increases.The negative values of Q_{ads} indicate adsorption of inhibitors, hence it supports physisorption mechanism.The negative values of ΔG_{ads} show that adsorption of inhibitor on surface of the Aluminium is spontaneous. Adsorption of PE on Aluminium obeys the Langmuir and Frumkin adsorption isotherms.AC impedance spectra reveal that a protective film is formed on the metal surface.The SEM micrographs confirm the formation of protective layers on the metal surface.

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